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RESULTS OF THE POLYMERIC FILMS SKYLAB D024 EXPERIMENT.(U)
AUG 75 W L LEHN, C J HURLEY
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SKYLAB DO24 EXPERIMENT

Elastomers and Coatings Branch
Nonmetallic Materials Division

August 1975

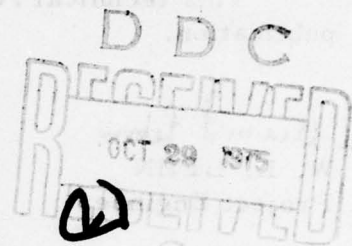
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Report for the period January 1968 - October 1974

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AIR FORCE MATERIALS LABORATORY
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measured changes in the optical, physical and electrical properties were due to a combination of excessive contamination, solar degradation of the contaminant layer and degradation of the polymer film materials. The degree of contamination experienced compromises the measurement of the degradation of the polymeric film themselves. Experimental results on the analysis of contamination are also presented.



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PREFACE

This report was prepared by the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. This work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734007, "Coatings for Energy Utilization, Control and Protective Functions", and was administered under the direction of the Air Force Materials Laboratory with Dr. William L. Lehn (AFML/MBE) Project Engineer.

This summary report covers a portion of the work on the evaluation of the DO24 polymeric films experiment hardware recovered from Skylab, SL 1/2, SL 1/3 and SL 4 and encompasses a period from January 1968 when the experiment was first being developed to October 1974. Additional summary reports covering other portions of the DO24 experiment hardware are in progress and will appear at a later date. It was submitted by the authors in January 1975.

Many of the materials used in this project were not developed or intended for the conditions to which they were subjected. Any failure or poor performance of a material is, therefore, not necessarily indicative of the utility of the material under less stringent conditions or for other applications.

The authors gratefully acknowledge the assistance of W. Glen, G. Clinehens, R. Vissoc, G. Stevenson, J. Schwarberg, R. Whittaker, J. Osseges, K. Fisch, and G. Ehlers.



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RESULTS OF THE POLYMERIC FILMS SKYLAB DO24 EXPERIMENT

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Abstract

Results of an experiment designed to evaluate the effects of the near earth environment on the performances and properties of selected polymeric films were exposed to the Skylab space environment for varying periods of time during the mission. The individual specimen holders were retrieved during EVA by the Astronauts, placed in hermetically sealed containers, recovered and returned to the Air Force Materials Laboratory for analysis and evaluation. Post flight analysis of the three sets of recovered polymeric films indicated measured changes in the optical, physical and electrical properties were due to a combination of excessive contamination, solar degradation of the contaminant layer and degradation of the polymer film materials. The degree of contamination experienced compromises the measurement of the degradation of the polymeric film themselves. Experimental results on the analysis of contamination are also presented.

I. Introduction and Background

Polymeric films find many uses in satellites and spacecraft as tapes, electrical and thermal insulation, as protective shrouds and covers and as components of multi layer thermal control coatings. The objective of the DO24 Polymeric Films experiment was to evaluate the effects of the near earth environment on selected polymeric films and provide correlation and calibration data for laboratory in situ space simulation. The data obtained would add new insight into mechanisms of degradation and improved damage theories and provide direction for the development of new and improved materials. The rationale behind the selection of the polymeric film materials for the DO24 experiment consisted of the following: (1) the materials would be of current interest; either being used by the aerospace community or promising materials under research and development. (2) The materials were to cover the broad spectrum of polymeric film materials with emphasis on polymeric films suitable as substrates for optical coatings. (3) For the purpose of correlation analysis, the selections were to include well characterized materials with respect to both ground based simulation testing and other flight materials. (4) The selection was to include materials both stable and unstable to the near earth environment. The unstable materials were to have known degradation characteristics with different regions of spectral and physical degradation.

The DO24 Polymeric Film flight hardware shown in Figure 1 consisted of two duplicate speci-

men trays each containing eight different polymeric film specimens. Pertinent properties of all specimens were individually measured prior to flight. The specimen trays along with two hermetically sealable return containers were mounted on the exterior of the Airlock Module (AM) near the Extravehicular Activity (EVA) hatch shown in Figure 2 prior to launch. The

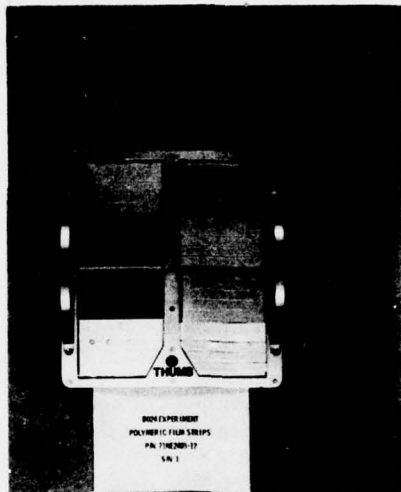


Figure 1. DO24 Polymeric Films Flight Hardware

DO24 FLIGHT EXPERIMENT

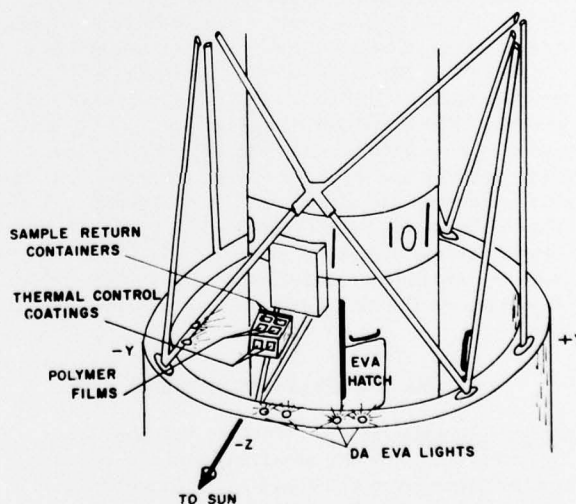


Figure 2. DO24 Flight Experiment

polymeric films were located some 39° off axis to the sun vector. The specimens were protected

during the launch phase by the payload shroud and were exposed after shroud ejection. Due to the passive nature and location of the experiment the mechanical and electrical problems experienced by Skylab during the initial phases of the flight due to the loss of the solar panel and workshop thermal shield had little or no direct effect on DO24. However, a more far reaching effect was the increased contaminant concentration added to the Skylab external environment as a result of the overheating of the workshop external surfaces and interior. This required the venting of that internal atmosphere prior to Astronaut occupancy plus the additional contamination resulting from the deployment of the sun shade and solar sail and fluid leak in the primary cooling loop. The specimen holders after exposure were removed and sealed in the return containers by the Astronauts during EVA and returned to earth for measurements and evaluation.

The first set of specimens, SL 1/2, were retrieved by the first crew of Skylab 2 (SL-2) astronauts after approximately 550 hours of solar exposure (35 days) and returned to earth for analysis. The second set of specimens, SL 1/3, were retrieved after approximately 2040 hours of solar exposure (131 days) and returned to earth for analysis. Post flight examination of the return containers shown in Figure 3 and the recovered materials specimens indicated that the materials had been exposed to a high level of contamination which had severely degraded in the solar space environment. The contamination tended to compromise the measurement of optical property degradation. The contamination was originally ascribed to the Service Module Reaction Control Systems (SMRCS) propellant by-products as a result of the fly by and docking maneuvers. An additional back-up set of specimen trays was approved for launch, deployment, exposure and retrieval on Skylab (SL-4) in an effort to preclude contamination effects. The specimens were deployed and recovered by the third crew of astronauts after approximately 1150 hours (74 days) of solar exposure. The third set of specimens, SL-4, experienced no SMRCS exposure, being deployed after docking and recovered before undocking, but still exhibited the effects of contamination. A set of pre-flight and recovered SL 1/3 Polymeric Film Specimen Holders are shown in Figure 4. Note the shading or shadowing effect of the retainer spring on the observed coloration contamination.

II. Optical Measurements

Optical Transmission. Pretest and post test transmission spectra measurements of the polymeric films from 0.25 μ m to 2.5 μ m were determined using a Beckman ratio recording spectrophotometer. Significant changes in the percent transmission occurred for most of the polymer materials. Post test transmission measurements on FEP Type A (Figure 5) and FEP Type XC20

(Figure 6) indicated the presence of an absorption edge at 0.6 microns not present in the original material. This is consistent with the changes in reflectance in the ultraviolet and visible regions observed for the thermal control coating materials flown as the companion experiment and previously reported.⁽¹⁾ Polyimide (Figure 7) and Polyphenylquinoxaline (PPQ) (Figure 8) post test measurements showed minimum change insofar as optical transmission was concerned.

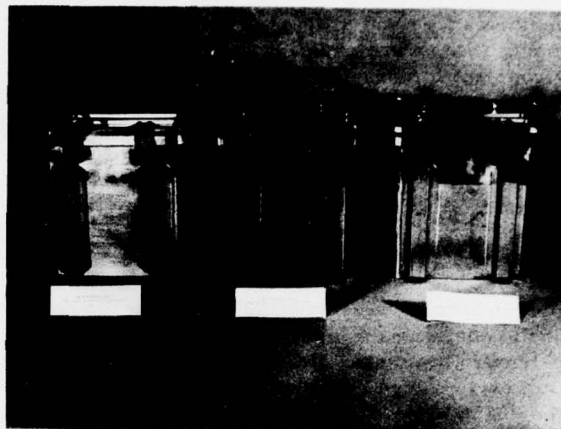


Figure 3. DO24 Specimen Holder Return Containers

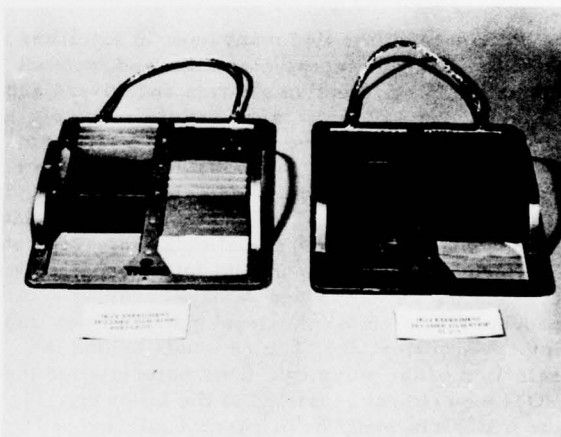


Figure 4. DO24 Polymeric Film Specimen Holder (Preflight and SL 1/3)

FMIR Spectra of Polymeric Films. Pre and post test FMIR spectra of the unexposed recovered flight experiment polymeric films were obtained using a Perkin Elmer 621 infrared spectrophotometer with a 45° KRS-5 FMIR prism. The FMIR spectra of the exposed front surfaces of the polymeric films indicated two noticeable effects. (1) The spectrum of each film was qualitatively similar to the spectrum of the original pretest polymeric films, although the intensity of the absorption bands was decreased for each film; this was indicative of a thin deposit on the exposed surface

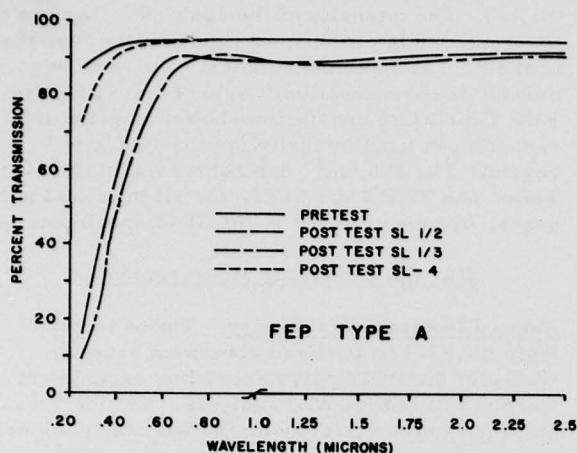


Figure 5. Effects of Skylab Space Environment Exposure on FEP Type A

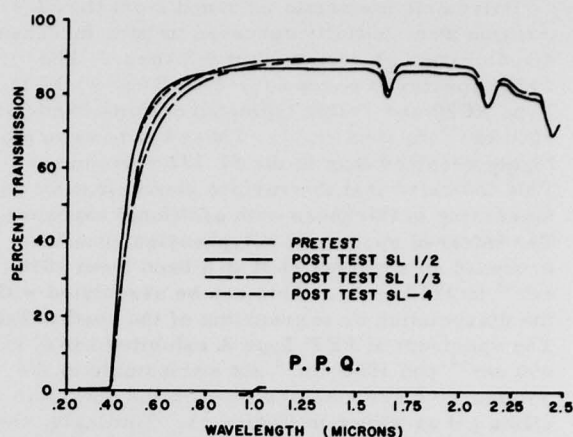


Figure 8. Effects of Skylab Space Environment Exposure on PPQ

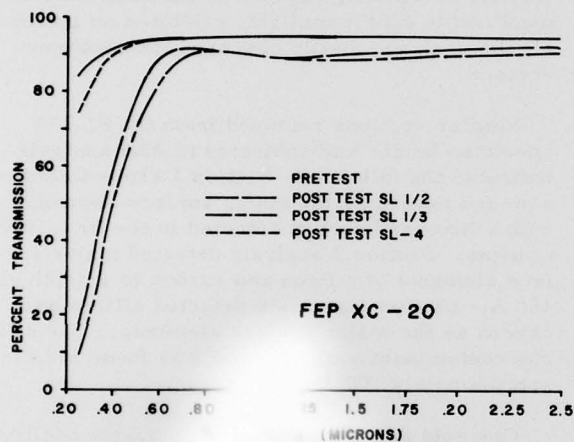


Figure 6. Effects of Skylab Space Environment Exposure on FEP XC-20

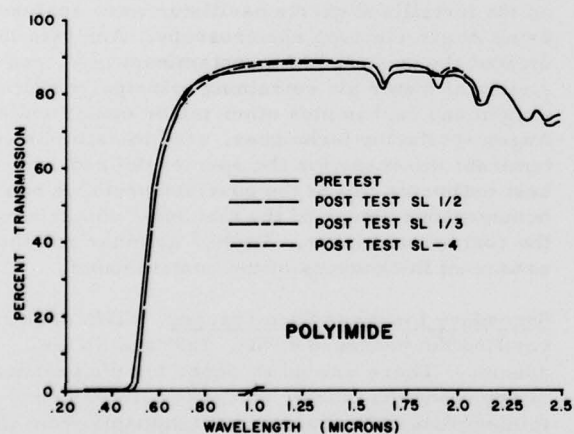


Figure 7. Effects of Skylab Space Environment Exposure on Polyimide

films. (2) An absorption band appears in each spectrum at approximately $1050\text{--}1100\text{ cm}^{-1}$ which can be attributed to a siliceous material.

Visual observation of the polymeric material returned from the SL 1/2 mission indicated a thin golden brown contaminant layer on all exposed surfaces of the experiment hardware except those areas shadowed from direct sunlight as shown in Figure 9. An absorption band appeared in each spectrum at about $1050\text{--}1100\text{ cm}^{-1}$ which corresponded to a band found in silica gel, $\text{SiO}_2\text{XH}_2\text{O}$. The SL 1/2 Nylon 6/6 specimen showed a new band at $1000\text{ to }1250\text{ cm}^{-1}$ resembling the KBR spectrum of silica gel as shown in Figure 10.

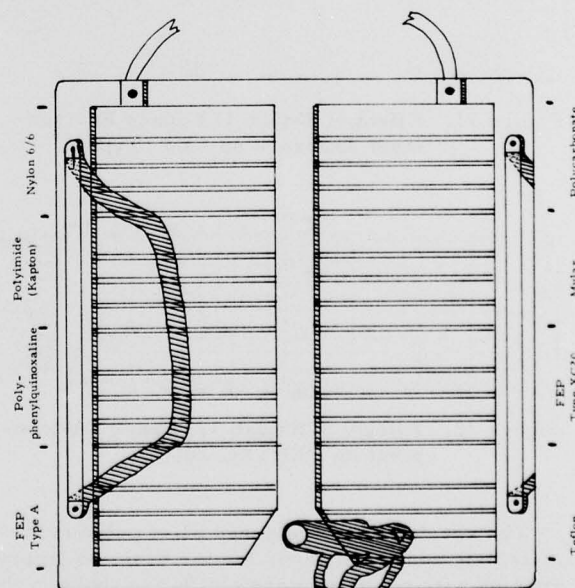


Figure 9. Shadow Pattern on Recovered SL 1/2 Polymer Film Experiment

Polymeric materials returned from the SL 1/3 mission were initially observed to have increased discoloration or contaminant thickness. The FMIR spectra of Nylon 6/6, FEP Type A, FEP Type XC20 and Teflon indicated definite bands at 1060 cm^{-1} to 1065 cm^{-1} . These bands were more highly resolved than in the SL 1/2 specimens. This indicated that the surface contamination was increasing in thickness with additional exposure. The infrared spectra of polyphenylquinoxaline produced an apparent shift in a band from 1050 cm^{-1} to 1110 cm^{-1} . This can be associated with the dissociation or degradation of the contaminant. The spectrum of FEP Type A exhibited bands at 450 cm^{-1} and 1060 cm^{-1} not attributable to the polymer and are also observed in the spectrum of silica gel as shown in Figure 11. Similarly, the post test spectra of FEP XC20 shown in Figure 12 and Teflon exhibited absorption at 450 cm^{-1} , 950 cm^{-1} and 1060 cm^{-1} where bands from $\text{SiO}_2\text{XH}_2\text{O}$ also appear.

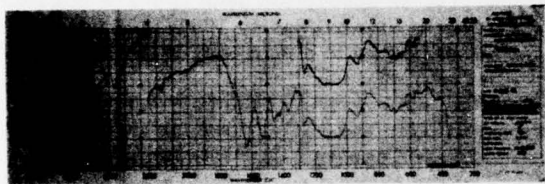


Figure 10. Effects of Skylab 1/2 Space Environment Exposure on Nylon 6/6

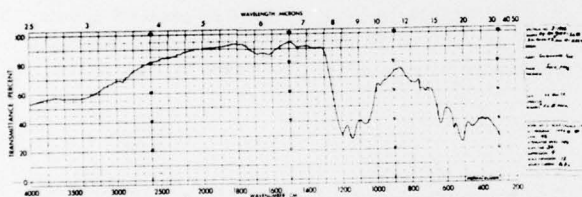


Figure 11. Effect of Skylab 1/3 Space Environment Exposure on FEP (Type A)

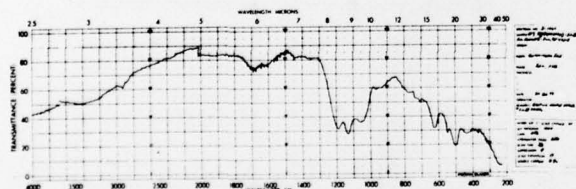


Figure 12. Effects of Skylab 1/3 Space Environment on FEP (XC-20)

The spectra of the returned SL-4 polymeric materials contained bands for the basic polymeric species with positions very similar to those in the spectra of the preflight test materials. Generally, the polymer absorption peaks in the SL-4 materials were of stronger intensity than those of

SL 1/3. The intensity of the 1060 cm^{-1} band in the SL-4 materials diminished significantly over that of the SL 1/3 specimens indicating a reduced amount of contamination. Nylon 6/6, FEP Type A, FEP Type XC20 and Teflon showed in general a reduction in band intensity for the 1060 cm^{-1} region. The 450 cm^{-1} band observed in the SL 1/3 Teflon and FEP Type XC20, for all practical purposes, has disappeared in the SL-4 specimens.

III. Spectroscopic Measurements

Auger Electron Spectroscopy. Three sections from the SL 1/2 anodized aluminum retainer spring of the DO24 polymeric films experiment were submitted for AES analysis. Section 1 was an area in face contact with the specimen holder frame. The analysis was typical of anodized aluminum with carbon contamination. Section 2, exposed to the local environment but protected from solar energy, exhibited a large silicon peak with an accompanying decrease in aluminum intensity. Section 3, exposed to the local environment and in direct sunlight, exhibited an increased silicon peak and totally obscured the aluminum surface.

Similar sections removed from the SL 1/3 specimen holder and subjected to AES analysis indicated the following: Section 1 showed aluminum and oxygen as the major surface elements with silicon and carbon detected in the first 100 Å of depth. Section 2 analysis detected major surface elements of silicon and carbon to a depth of 150 Å. Section 3 analysis detected silicon and oxygen as the major surface elements. The silicon contaminant surface layer was found to be approximately 300 Å in thickness.

One gold and one silver coated quartz oscillator were mechanically mounted on the companion thermal control coatings experiment adjacent to the polymeric films experiment to serve as contamination monitors during the exposure of the various specimen holders. The contaminant layer on the metallized quartz oscillator were analyzed using Auger electron spectroscopy. Analysis indicated the presence of a contaminant layer consisting of materials containing principally silicon, oxygen and carbon plus other minor constituents. Auger sputtering techniques, used to estimate contaminant thickness for the species defined, are best estimates due to the possible/probable non homogeneous nature of the materials comprising the contaminant layer. Table 1 summarizes the estimated thicknesses of the contaminants.

Secondary Ion Mass Spectroscopy. SIMS analysis verified the presence of Si^+ , SiO^+ and SiOH^+ species. There was no evidence for the presence of any other than minor traces of nitrogen containing materials expected contaminants from the reaction control system, or for the presence of any methyl silicone groups or fragments. Presence of the latter were predicted to be the major

TABLE 1
AUGER ANALYSIS OF DO24 EXPERIMENT CONTAMINATION

Specimens	SL 1/2		SL 1/3		SL-4	
	Element	Deposit Å	Element	Deposit Å	Element	Deposit Å
Gold Coated Quartz Crystal Oscillator	Si	1700	Si	250	Si	100
	O	1700	O		O	150
	C	700	C	40	C	
Silver Coated Quartz Crystal Oscillator	Si	2450	Si	75	Si	100
	O	2450	O	75	O	
	C	700	C		C	100
			N	Trace		
Anodized Aluminum	Si	+	Si	300	Si	
Retainer Spring	O	+	O	175	O	
(Section 3)	C	+	C	600	C	

contaminants for the DO24 experiment as a result of the outgassing from the S-13G thermal control coating used on the back side of the ATM solar panel. The back side of this panel presents the best line of sight contaminant source for DO24. Efforts to determine the nature of the contamination by mass spectroscopy gave negative results and indicated that the material was essentially non volatile.

IV. Physical Measurements

Differential Scanning Calorimetry (DSC). Many polymers undergo a change of state called the glass transition (T_g) when their temperature is raised. The transition is identified by substantial changes in the properties of the polymer. The DSC determinations were performed at $\Delta T = 20^\circ\text{C}/\text{min}$ with the specimens in crimped specimen holders and a nitrogen flow of $\sim 20 \text{ cc}/\text{min}$. As a criterion for the glass transition temperature, the extrapolated onset of the baseline shift was used, whenever possible, while a weak endo or exothermic peak, or a "knee" in the curve, had to be used in cases where the onset could not be defined easily or reproducibly. Two first order transitions in Teflon and the crystalline melting points were identified using the (endothermic) peak temperature. Assignment of the transitions was straight forward, based on information from our transition file. No transitions of any kind were found for the Polyimide. The transitions represent averages of 2 to 4 specimens. Reproducibility was very good, with the exception of the T_g values of the FEP specimens and one set of Mylar data.

As previously stated all materials darkened during space exposure and Nylon, Polycarbonate and Mylar became noticeably stiffer after exposure on SL 1/2. While the specimens showed little or no change in the T_g and the melting point (T_m) after the SL 1/2 space exposure, most specimens had increased T_g's and/or T_m's after the SL 1/3 space exposure. The increase amounted to 10 to 13°C in most cases and very likely is the result of free radical formation and subsequent crosslinking. Nylon 6/6 did not show any change in T_g or T_m, although the material after SL 1/2 space exposure, was distinctly stiffer at room temperature, i.e., below the glass transition temperature. For the very rigid polymers, such as Polyimide, the methods for determination of T_g were not sensitive enough. For this particular Polyimide a T_g around 380°C would have been expected and might have been raised as a result of space exposure.

In general, the SL-4 data lies between the values obtained for SL 1/2 and SL 1/3. Figure 13 and 14 show the trend of change for the glass transition temperature and for the crystalline melting points. As can be seen, the crystalline melting points increase with increasing space exposure, with the exception of Nylon 6/6 which remains essentially unchanged. The glass transition temperature of PPQ, Mylar and Polycarbonate also show an increase while those of Nylon 6/6 and FEP films remain essentially unchanged.

Tensile Properties. Pretest and post test tensile measurements generally indicated the degree of polymer crosslinking and/or degradation of the polymeric film materials. Nylon 6/6 exhibited

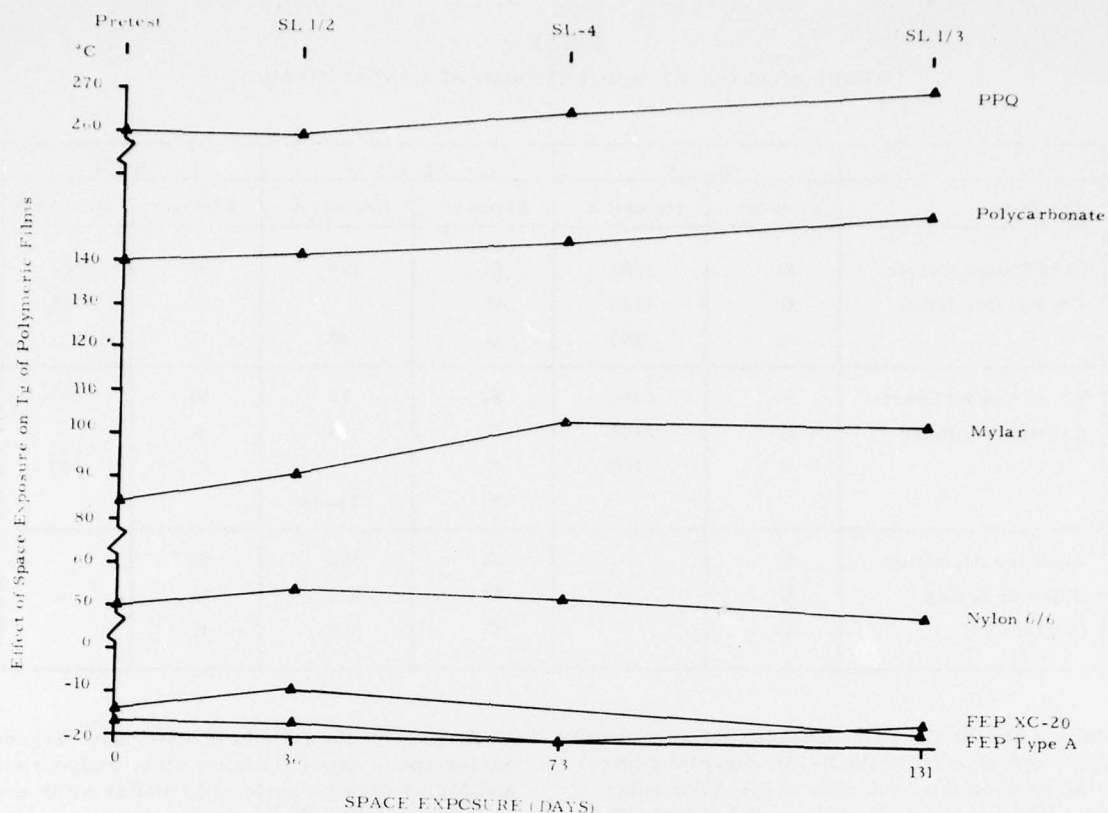


Figure 13. Change in Glass Transition Temperature vs Duration of Exposure

significant reductions in percent elongation and increases in modulus indicating progressively increased polymer crosslinking. Polyimide showed moderate changes in the percent elongation and slight variations in modulus and a progressive reduction in tensile strength consistent with polymer degradation. Variations in percent elongation and modulus for PPQ with progressive reductions in tensile strength indicate an initial polymer crosslinking and subsequent moderate degradation. Initial percent elongation reductions followed by reduction in tensile strength indicate slight degradation accompanied by mild crosslinking for FEP Type A. Polycarbonate exhibited reductions in percent elongation and tensile strength pointing to slight to moderate degradation. Significant reductions in percent elongation and tensile strength of Mylar with the onset of reduction in yield strength indicate simultaneous degradation and crosslinking. FEP XC20 exhibited reductions in percent elongation and increases in modulus indicating progressively mild to moderate crosslinking. Extreme reductions in percent elongation and tensile strength with moderate variations in modulus indicate that Teflon suffered increasing degradation and a slight degree of crosslinking. Tables 2 through 5 present this change exhibited by all the polymeric materials exposed during the three

missions.

Dielectric Measurements. Measurements of dielectric strength, dielectric constant and loss tangent factor of the pretest flight materials were made. Post flight measurements of dielectric properties could not be interpreted due to complications arising from the dielectric contaminant on the exposed surface of the recovered flight materials.

V. Results and Discussion

Initial optical measurements, as well as visual observation, of the returned DO24 specimens indicated a severe contamination problem. CSM flyby photographs provided evidence of excessive contamination localized to an area on the EVA side of the MDA extending up to and including the ATM structure. Persistent efforts have been made to identify the nature as well as the source of the contaminants.

Receiving inspection of the returned DO24 SL 1/2 and SL 1/3 containers indicated severe contamination during exposure in space. The distinct shadow patterns on the return containers and those observed later after opening the containers on the

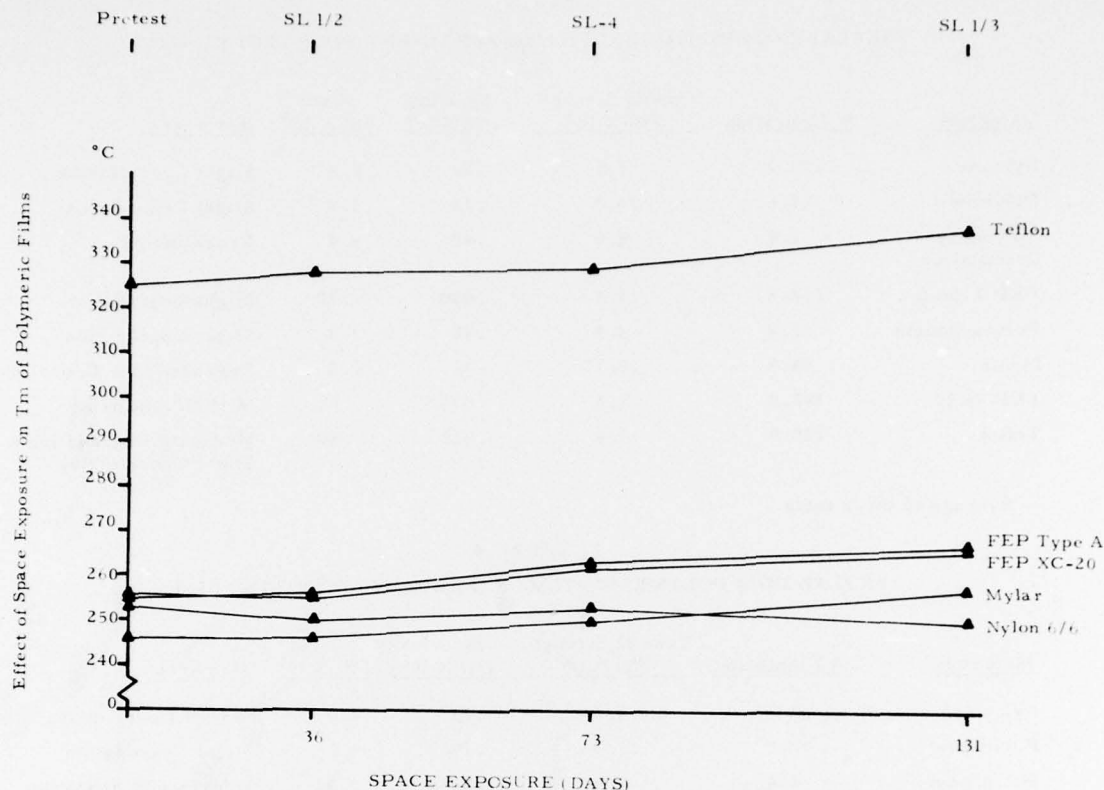


Figure 14. Change in Crystalline Melting Points vs Duration of Exposure

TABLE 2
SKYLAB DO24 POLYMERIC FILMS EXPERIMENT PRETEST DATA

Materials	% Elongation	Tensile Strength PSI X 10 ³	Modulus PSI X 10 ⁶	Yield PSI X 10 ³	Remarks
Nylon 6/6	191.5	5.1	.075	1.9	
Polyimide	55.5	13.9	.18	4.6	
Polyphenyl Quinoxaline	6.6	8.2	.20	3.8	
FEP Type A	231.0	2.0	.03	.75	
Polycarbonate	* 91.1	5.8	.13	3.3	
Mylar	74.8	14.5	.30	6.3	
FEP XC20	220.5	1.8	.02	.62	
Teflon	365.8	2.9	.022	.60	

* Average of three tests

specimen holders gave a clear indication of the excessive contamination and degree to which it had been degraded by solar exposure. Clarity and definition of the shadow patterns shows excellent consistency with the expected solar angle of exposure for the experiment.

Post test optical transmission measurements showed significant changes in ultraviolet transmission for Nylon 6/6, Teflon TFE,⁽²⁾ Polycarbonate, Mylar Type A, FEP Type A and FEP XC 20. The FEP materials shown in Figures 5 and 6, in particular, because of their original high transmission in the ultraviolet indicate the presence of

TABLE 3
SKYLAB DO24 POLYMERIC FILMS EXPERIMENT POST TEST SL 1/2

<u>Materials</u>	<u>% Elongation</u>	<u>Tensile Strength PSI X 10³</u>	<u>Modulus PSI X 10⁶</u>	<u>Yield PSI X 10³</u>	<u>Remarks</u>
Nylon 6/6	173.1	5.6	.12	2.8	Slight Crosslinking
Polyimide	* 44.6	11.3	.16	3.9	Slight Degradation
Polyphenyl Quinoxaline	1.9	8.0	.48	5.4	Crosslinking
FEP Type A	218.3	1.5	.030	.70	Slight Degradation
Polycarbonate	52.4	4.5	.15	3.4	Slight Degradation
Mylar	48.3	10.7	.32	6.2	Degradation & Crosslinking
FEP XC20	192.8	1.4	.038	.52	Mild Crosslinking
Teflon	220.8	1.9	.029	.40	Moderate Degradation & Slight Crosslinking

* Average of three tests

TABLE 4
SKYLAB DO24 POLYMERIC FILMS EXPERIMENT POST TEST SL 1/3

<u>Materials</u>	<u>% Elongation</u>	<u>Tensile Strength PSI X 10³</u>	<u>Modulus PSI X 10⁶</u>	<u>Yield PSI X 10⁶</u>	<u>Remarks</u>
Nylon 6/6	49.3	5.1	.23	4.0	Severe Crosslinking
Polyimide	37.2	11.3	.19	3.2	Slight Degradation
Polyphenyl Quinoxaline	4.4	6.5	.215	4.0	Moderate Degradation
FEP Type A	224.5	1.9	.037	0.7	Mild Crosslinking
Polycarbonate	53.9	4.5	.16	3.2	Slight Degradation
Mylar	* 12.9	8.1	.31	5.8	Degradation & Crosslinking
FEP XC20	248.0	1.6	.035	0.7	Increased Crosslinking
Teflon	105.8	1.2	.04	0.7	Increased Moderate Degradation & Slight Crosslinking

* Average of three tests

TABLE 5
SKYLAB DO24 POLYMERIC FILMS EXPERIMENT POST TEST SL-4

<u>Materials</u>	<u>% Elongation</u>	<u>Tensile Strength PSI X 10³</u>	<u>Modulus PSI X 10⁶</u>	<u>Yield PSI X 10⁶</u>	<u>Remarks</u>
Nylon 6/6	31.24	5.20	.143	2.63	Severe Crosslinking
Polyimide	38.7	12.19	.188	2.45	Moderate Degradation
Polyphenyl Quinoxaline	5.99	7.4	.216	3.38	Moderate Degradation & Crosslinking
FEP Type A	196.9	1.26	.028	.58	Moderate Crosslinking & Slight Degradation
Polycarbonate	11.72	4.51	.145	2.10	Degraded more than SL 1/2 and SL 1/3
Mylar	5.69	5.34	.239	3.40	Degradation and Increased Crosslinking
FEP XC20	212.08	1.31	.0335	.67	Moderate Crosslinking
Teflon	39.7	0.925	.0355	.72	Increased Degradation and Less Crosslinking than SL 1/2 and SL 1/3

a degraded contaminant with an absorption edge at 0.6 microns. The spectra of Polyimide and PPQ shown in Figures 7 and 8 indicate little, if any, effect of ultraviolet transmission for these materials. Degradation of the contaminant by ultraviolet is consistent with the changes in reflectance/absorptance observed for the companion thermal control coatings materials. The changes in optical transmission due to the contaminant do appear to coincide with contaminant thickness layer and duration of exposure to solar energy.

Visual observation of the polymeric film specimens returned from the SL 1/2, SL 1/3 and SL-4 missions indicated the presence of clear image patterns of the specimen holder retainer spring, pip pin and pip pin cable. The location of these image patterns were consistent with the 39° off axis to the sun vector as was shown in Figure 9. These observations further confirm the presence of a highly mobile contaminant which severely degraded when directly exposed to solar energy.

Analysis of the FMIR spectra of all the polymeric film specimens returned from the Skylab missions were qualitatively similar to the spectrums of the original pretest materials, although the intensity of the background absorption bands were decreased for each of the films materials. In addition, an absorption band appeared in each spectrum at approximately $1050-1100\text{ cm}^{-1}$ which was attributed to a siliceous material layer on the post flight specimens. Review of the spectra indicated a resemblance to the KBR spectrum of silica gel, $\text{SiO}_2\text{XH}_2\text{O}$, which has absorption bands at 450, 950 and 1060 cm^{-1} . All of these absorption bands were present in the post flight FEP XC20 and Teflon and are not attributable to the original polymeric material. Variations in absorption band intensities of the post flight polymeric materials indicate significant differences in contaminant concentration with this chemical functionality for each of the three missions. The SL 1/3 post flight polymeric specimens exhibited the highest degree of contamination. The SL-4 recovered materials had a lower concentration of contamination than SL 1/2 and SL 1/3 specimens. This is consistent with the duration of each flight exposure and with a reduction in concentration of residual contamination during the final mission period.

Post test measurement of the tensile properties provide the most obvious evidence of polymer degradation and crosslinking. By example, Nylon 6/6 exhibited progressive crosslinking dependent on solar energy radiation total dose. FEP Type A performed about as expected, showing the least amount of change in physical properties.⁽³⁾ It must be noted the SL-4 post flight materials exhibited increased degradation and crosslinking over the post flight SL 1/3 materials. In the former case, the materials were subjected to approximately 50% of the exposure time and less than 50% of the contamination thickness.

Results of the DSC measurements indicate the anticipated trends of polymeric materials subjected to a solar radiation environment. An unstable energy condition as a result of radiation exposure gives rise to broken bonds and unpaired electrons resulting in free radical formation. Additionally, ions are produced. The recombination of radicals and ions may result in gradually changing the physical-mechanical properties of the polymeric films.

Measured changes in transmission indicate an essentially uniform contaminant layer over all exposed surfaces of the experiment. The sharpness of the shadow patterns indicate that the contaminant was degraded and fixed by solar radiation. Absence of any noticeable amount of contaminant in areas facing in opposing directions to solar radiation indicate a high degree of mobility. Consequently, the contaminant was able to deposit and reevaporate or migrate over the surface prior to being fixed by solar radiation. The measured increase in contaminant thickness found between SL 1/2 and SL 1/3 is in accord with a volatile contaminant which can reevaporate after initial deposition unless it is fixed by solar radiation. The increase in observed optical degradation is the result of further degradation and color formation in the non volatile fixed contaminant.

The Auger and SIMS analysis in combination with other results and observations also point toward a volatile silicon and oxygen containing contaminant. Absence of any carbon to silicon fragments in the SIMS analysis, the lack of any C-methyl in the mass spectroscopy analysis and the evidence for the presence of SiO bands in the FMIR similar to those found in silica gel also point to volatile SiO containing contaminants which can undergo volatilization and condensation and in the presence of solar radiation give a non-volatile, ultraviolet unstable siliceous material.

In the main, comparisons with ground based simulations of the solar vacuum environment were not distinguishable. Review of available data did indicate a similarity in trends of degradation, if one considers the effect of contamination on the total energy incident on the surface. It is evident from this data obtained that under conditions which include the consideration of contamination valid data might be obtained. Future spacecraft will continue to utilize polymeric materials in a wide variety of internal and external applications. Data from recovered flight experiments can be used to guide the development of new and improved materials which will provide an expanding range of materials available to the spacecraft designer.

VI. Contamination Hypothesis

Based upon the results and data generated the following contamination hypothesis is offered to explain the observed results and to account for

the localized contamination noted in the DO24, MDA and ATM area.

During the manned phases of each of the Skylab missions leakage of the primary cooling loop working fluid, Coolanol-15, a volatile silicate ester was noted. The location of the leak has not been determined, but appears to have occurred in the EVA quadrant area. In fact, loss of material was such that resupply and recharging of the coolant loop was necessary and was accomplished by the SL-4 Astronauts. A leak in the secondary loop was reported. Contact of the silicate ester coming from a leak in the primary coolant loop with the external surfaces of the DO24 experiment area is postulated. In the presence of the solar energy and specifically in the presence of water vapor, contained in the external Skylab environment, this material would undergo vapor or surface hydrolysis to give an essentially nonvolatile hydrolysis product. The volatile alcohol by-product would be lost by vaporization. This initial hydrolysis product would through further stepwise hydrolysis, condensation, and loss of alkoxy groups and eventually be transformed into a non volatile impure silica gel-like material. Impure, nonstoichiometric silicon-oxygen materials of this nature are known to undergo ultraviolet degradation and color formation developing a clear, golden yellow to a deep brown.⁽⁴⁾ These materials similarly display an ultraviolet absorption edge near 0.6 microns. In the course of the combined hydrolysis/radiation damage process the contaminant might be expected to pass through an intermediate phase wherein the material might be free to migrate about the surface. However, under the influence of the solar radiation the exposed material would undergo more rapid reaction with the result that contaminant build up would occur in these areas exposed to the solar energy as material migrated from shadowed into exposed areas and give a fixed colored contaminant pattern. Unexposed areas would, therefore, have a much thinner layer of contamination and in the absence of radiation would not be discolored. The observed Auger analysis, visual observations, and analytical results are in accord with this proposed contamination scheme. The lesser degree of contamination/optical property degradation observed on the SL-4 thermal control coatings is in accord with the lower rate of coolant fluid leak observed during that portion of the Skylab mission. Due to a finite vapor pressure, reevaporation, one would not expect to find Coolanol-15 per se on any of the exposed surfaces of DO24.

It is felt that the results observed are not consistent with a contamination scheme in which the primary contaminant is volatile methylsilicone outgassing products from S-13G paint on the backside of the ATM solar array. Such a scheme would be consistent only if a radiation induced demethylation of the methylsilicone could be shown to occur.

VII. Conclusions

Changes in polymeric properties resulting from space flight ultraviolet radiation exposure can be predicted. Effects of contamination, if present, must be taken into consideration.

Localized contamination effects from multiple and varied sources may be present in large systems which do not integrate directly into an overall contamination model and must be considered individually.

A localized contamination hypothesis has been proposed to explain the results observed on the Skylab DO24 Experiment.

The recovery of materials specimens from space experiments in sealed containers, free of exposure to the recovery environment, provides a useful means of obtaining space exposure induced optical and physical properties degradation.

Measurements of the optical changes in the exposed surface layers and bulk of the polymeric films were largely compromised due to the excessive contamination. However, significant information relative to the identity of the contaminants and the overall Skylab contamination analysis were obtained.

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